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Wafer-Scale Assembly of Highly Ordered Semiconductor Nanowire Arrays by Contact Printing

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ABSTRACT

Controlled and uniform assembly of "bottom-up" nanowire (NW) materials with high scalability presents one of the significant bottleneck challenges facing the integration of nanowires for electronic applications. Here, we demonstrate wafer-scale assembly of highly ordered, dense, and regular arrays of NWs with high uniformity and reproducibility through a simple contact printing process. The assembled NW pitch is shown to be readily modulated through the surface chemical treatment of the receiver substrate, with the highest density approaching ~8 NW/μm, ~95% directional alignment, and wafer-scale uniformity. Such fine control in the assembly is attained by applying a lubricant during the contact printing process which significantly minimizes the NW–NW mechanical interactions, therefore enabling well-controlled transfer of nanowires through surface chemical binding interactions. Furthermore, we demonstrate that our printing approach enables large-scale integration of NW arrays for various device structures on both rigid silicon and flexible plastic substrates, with a controlled semiconductor channel width ranging from a single NW (~10 nm) up to ~250 μm, consisting of a parallel array of over 1250 NWs and delivering over 1 mA of ON current.

In recent years, synthetic nanomaterials, such as carbon nanotubes and semiconductor nanowires, have been actively explored as the potential building blocks for various electronic applications as they offer advanced properties arising from their miniaturized dimensions.[1−11] For instance, they may enable further scaling of the devices down to the molecular regime with enhanced performances[2−7,10,11] while enabling new functionalities and therefore leading the way to novel technological applications[1,8,9,12−15] However, inarguably, one of the most significant challenges still facing the bottom-up approach is the large scale assembly of the nanomaterials at well-defined locations on substrates with high reproducibility and uniformity. Much effort has focused on tackling the controlled assembly,[12,13,16−26] and while significant progress has been made, it still remains an unresolved obstacle. Here, we present a novel and yet simple strategy for wafer scale assembly of highly ordered and aligned NW arrays on substrates with controlled pitch and density for electronic applications. The method is based on a simple contact printing process that enables the direct transfer and positioning of NWs from a donor substrate to a receiver chip. The process is compatible with a wide range of receiver substrates, including Si and flexible plastics. The dynamics and the mechanism of this transfer process are also explored through a series of systematic studies that has enabled us to gain further control over the NW assembly.

Our contact printing method involves directional sliding of a growth substrate, consisting of a dense "lawn" of NWs, on top of a receiver substrate coated with lithographically patterned resist (Figure 1a and Supporting Information). During the process, NWs are in effect combed by the sliding step and are eventually detached from the donor substrate as they are anchored by the van der Waals interactions with the surface of the receiver substrate, resulting in the direct transfer of aligned NWs to the receiver chip. An important aspect of this strategy, as compared to our previously reported dry transfer method,[13] is the use of octane and mineral oil (2:1, v:v) mixture as a lubricant during the transfer process. The lubricant serves as a spacing layer between the two substrates and minimizes the NW−NW friction during the sliding process. Such friction enhances the uncontrolled breakage and detachment of NWs while hampering the alignment (see Supporting Information, Figure S1). By minimizing the mechanical friction, well-controlled transfer of NWs is enabled through chemical binding interactions

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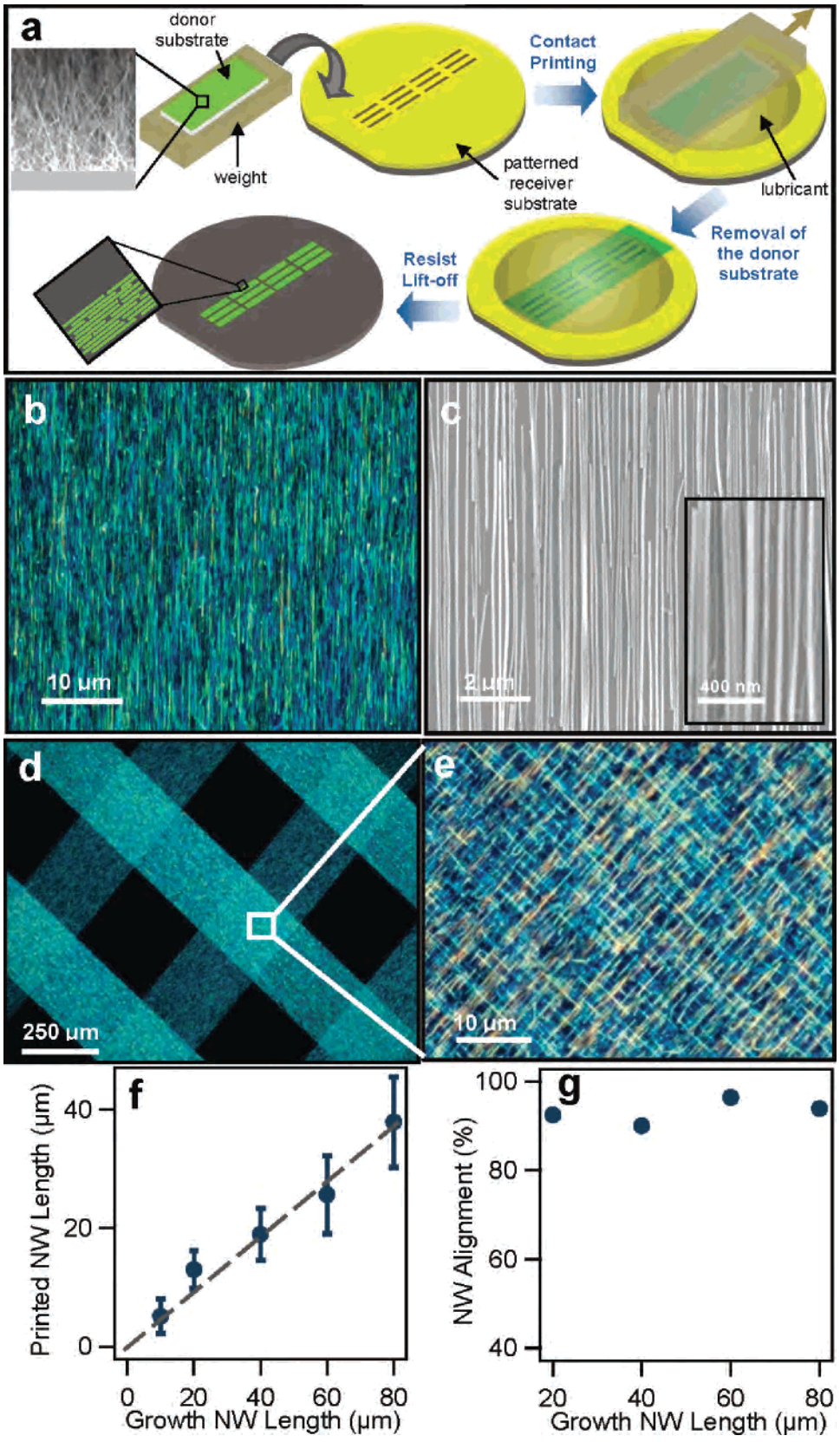

Figure 1. Contact printing of NWs. (a) Schematic of the process flow for contact printing of nanowire arrays. (b) Dark-field optical and (c) SEM images of GeNWs ($d \sim 30$ nm) printed on a Si/SiO_2 substrate showing highly dense and aligned monolayer of nanowires. The self-limiting process limits the transfer of NWs to a single layer, without significant NW bundling. (d) and (e) optical images of double layer printing for SiNW ($d \sim 30$ nm) cross assembly. (f) Average length of the printed nanowires as a function of their original length on the donor substrate, showing a linear trend with a slope of ~0.5. (g) The percentage of the aligned nanowires on the receiver substrate for various NW lengths. A nanowire is considered misaligned if its axis forms an angle >5° with respect to the printing direction.

between NWs and the surface of the receiver substrate. As a result, the printed NW density is readily modulated and tuned by the appropriate surface chemical modification which is highly desirable for meeting the needs of various NW-based applications. After NW printing, the patterned resist is removed by a standard lift-off process using acetone, leaving behind the nanowires that were directly transferred to the patterned regions of the substrate. The process is highly generic for a wide range of NW materials, including Si, Ge, and compound semiconductors, and for the entire NW diameter range, $d = 10-100$ nm, that was explored in this study.

The optical and scanning electron microscopy (SEM) images of assembled GeNWs on a Si/SiO_2 (50 nm, thermally grown) receiver substrate are shown in parts b and c of Figure 1, clearly demonstrating the uniformity of the well-aligned NW films. The transferred NWs form a single layer without any significant multilayer stacking (Figure 1c) which is attributed to the weak interactions between the chemically unmodified NWs. This rationale is further supported by the SEM observations showing no bundling of the as-grown nanowires on the donor substrate (Figure 1a, inset). Therefore, the printing process is self-limiting with the transfer of NWs restricted to a monolayer. The untransferred NWs remain on the donor substrate as evident from optical microscopy and SEM observations.[27] A self-limiting and directional assembly process is highly desirable for various electronic applications where uncontrolled vertical stacking of the wires can result in reduced gate coupling and, therefore, switching performances. In order to achieve controlled stacking of the wires, a multistep printing methodology was developed as demonstrated in parts d and e of Figure 1 where Si nanowire crosses are enabled through a two-step process. First, a layer of SiNW parallel arrays was printed on a receiver substrate. The sample was then spin-coated with a thin film of poly(methyl methacrylate) (PMMA, ~40 nm thick) or Shipley 1805 (diluted in PGMEA, ~40 nm thick) to serve as a buffer layer, followed by a second printing step normal to the direction of the first layer. Finally, the polymer buffer layer was etched away by a mild O_2 plasma process (60 W, 2 min), resulting in the assembly of large arrays of NW crosses. The controlled assembly of the NW crosses is of particular interest for novel optoelectronic applications enabled via heterogeneous integration of p- and n-type NW materials.[28,29] The printed NW crosses further demonstrate the versatility of the contact printing methodology presented here for hierarchical assembly of the bottom-up nanowires into a variety of geometric structures.

To quantitatively characterize the printed NW films, statistical analyses were conducted for the length and the alignment of the printed NWs. We observed that the average length of the printed NWs linearly increases with the length of the donor substrate nanowires (Figure 1f), approaching ~40 μm for a donor NW length of ~80 μm. We also achieve a high degree of alignment in the printed NW films. As shown in Figure 1g, >90% of NWs are highly aligned in the direction of sliding without any significant sensitivity to

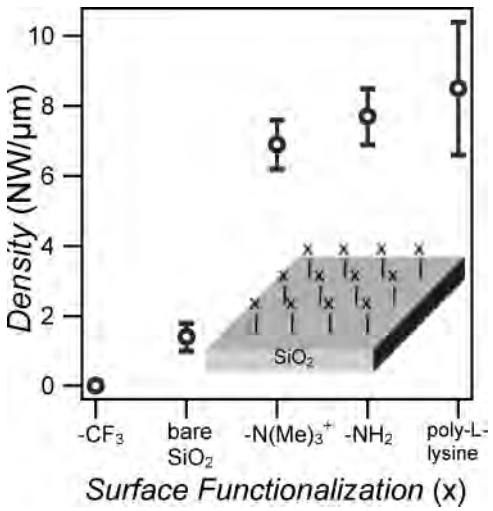

Figure 2. Nanowire printing density modulation by receiver substrate surface functionalization. GeNWs ($d \sim 15$ nm) were used for this study with a Si/SiO_2 receiver substrate. Bare SiO_2 corresponds to using the untreated substrate while $-CF_3$ ((heptadecafluoro-1,1,2,2-tetrahydrodecyl)dimethylchlorosilane), $-N(Me)_3^+$ (*N*-trimethoxysilylpropyl-*N*,*N*,*N*-trimethylammonium chloride), and $-NH_2$ (3-triethoxysilylpropylamine) correspond to the surface-modified functional groups (see Supporting Information). Note that, as expected, poly-L-lysine functionalization results in a larger standard deviation due to the less uniform coverage of the surface by the polymer thin film as compared to the monolayers.

the NW length. A NW was considered to be misaligned if its axis formed an angle >5° with respect to the sliding direction.

To shed light on the transfer mechanism and the process dynamics, and to gain further control over the printing process, we explored the role of surface chemical modification of the receiver substrate on the density of the printed NWs. Figure 2 shows the printed density of as-grown GeNWs (chemically unmodified, $d \sim 15$ nm) on chemically modified SiO_2 receiver substrates with various siloxane monolayers[9,30] as well as poly-L-lysine thin films (see Supporting Information). For the $-CF_3$ terminated monolayers, we observed almost no transfer of nanowires ($<10^{-3}$ NW/μm) from the donor to the receiver chip while an identical printing process on $-NH_2$ and $-N(Me)_3^+$ terminated monolayers resulted in a high density of transferred nanowires, approaching ~8 NW/μm. Such a major density modulation of ~4 orders of magnitude demonstrates the key role of the surface interactions on the printing outcome. Fluorinated surfaces are well-known to be highly hydrophobic and "nonsticky", therefore minimizing the adhesion of NWs to the receiver substrate during the sliding process. As a result, the wires remain rather unbroken on the donor substrate without being transferred to the receiver chip. On the other hand, $-NH_2$ and $-N(Me)_3^+$ terminated surfaces interact effectively with the NW surface[20] to yield a high-density transfer through strong bonding interactions. This demonstrates that our transfer process requires strong NW to receiver substrate interactions, which eventually results in the detachment of the wires from the donor substrate and the direct transfer to the receiver substrate during the sliding step. Notably, when the contact printing is carried out without

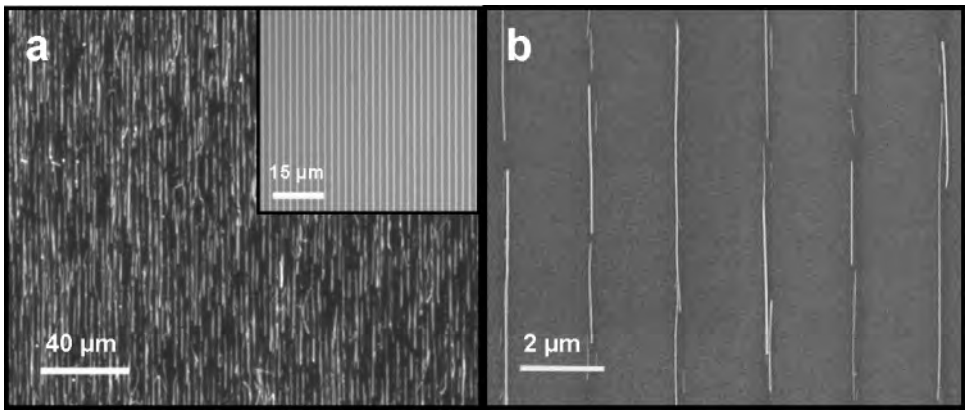

Figure 3. Single nanowire printing. (a) Optical and (b) SEM images showing regular array assembly of single GeNWs ($d \sim 30$ nm) at predefined locations on a Si/SiO_2 substrate. The inset in (a) shows an optical image of the e-beam patterned receiver substrate prior to the contact printing, consisting of an array of ~200 nm wide lines on a PMMA resist.

the use of lubricant, dramatically lower density contrast is observed for the various surface treatments, which hints that the use of lubricant is essential for gentle and controlled transfer of highly aligned NWs by lowering nonselective mechanical friction (see Supporting Information, Figure S1). In the future, it may be possible to further enhance the attained NW density through complementary surface functionalization of NWs and the receiver substrate.

The potency of our contact printing process is further demonstrated through successful assembly of regular arrays of single NWs at predefined locations on the substrate. To precisely control the location of single nanowires during the printing, arrays of lines with ~200 nm width and 2 μm pitch (Figure 3a inset) were defined on a PMMA resist with electron beam lithography (JEOL 6400, NPGS). The patterned substrate was then functionalized with a $-NH_2$ terminated monolayer to increase its adhesion to NWs. The followed GeNW printing and PMMA lift-off in acetone yielded a regular array of highly ordered single NWs with a 2 μm period as depicted in Figure 3. The patterned line width of ~200 nm that is required to achieve single NW trapping corresponds well to the average NW pitch of ~130 nm for the same NW material and surface treatment (Figure 2). Importantly, our contact printing process is highly scalable. We successfully assembled highly aligned and dense (~7 NW/μm) nanowire parallel arrays on a 4 in. Si wafer (with 50 nm SiO_2 functionalized with amine-terminated monolayer) as shown in Figure 4. The parallel array NW films, appearing as gray strips in the optical photograph, show a very uniform color contrast across the entire wafer which is a strong indication of the uniform density and alignment of the assembled NWs. While the density of the NW films that are obtained by the Langmuir−Blodgett (L-B) method[21,25] is comparable or slightly higher than those attained by our contact printing process, compared to other previously reported scalable assembly methodologies, such as the bubble blown technique where a maximum density of ~0.3 NW/μm was reported,[17] our contact printing method enables ~20× improvement in the NW density. A high NW density is desirable for achieving dense arrays of single NW devices, or high ON currents in the case of thin film transistors with parallel array NW channels.

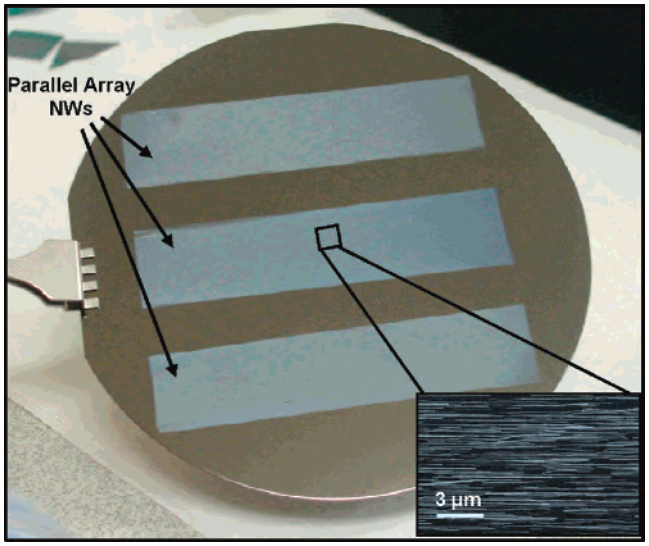

Figure 4. Wafer-scale nanowire printing. Large area and highly uniform parallel arrays of aligned GeNWs ($d \sim 30$ nm) were assembled on a 4 in. Si/SiO_2 wafer by contact printing. The inset is an SEM image of the printed NW film, showing a density of ~7 NW/μm.

The ability to uniformly assemble both single and highly dense parallel arrays of NWs on substrates and in large scale leads the way for exploring a wide range of electronic device structures based on NWs. This is of paramount importance since various applications have different criteria for the desired device characteristics, for example some demanding high density while others requiring high current drives. In order to explore the feasibility of our contact printing strategy for various electronic structures, we have studied the effect of channel width scaling on the device performance and characteristics. High mobility core/shell Ge/Si (~15/5 nm) NWs[13,31,32] were printed into regular arrays and configured as back-gated field-effect transistors (FETs) by defining Ni/Pd (5/45 nm) source (S) and drain (D) contacts with channel widths ranging from a single NW (~30 nm) up to ~250 μm (Figure 5a) and a channel length of ~2 μm. The average ON current of NW FETs as a function of the channel width, and therefore the number of NWs per channel, is shown in Figure 5b. It can be clearly seen that the ON current linearly

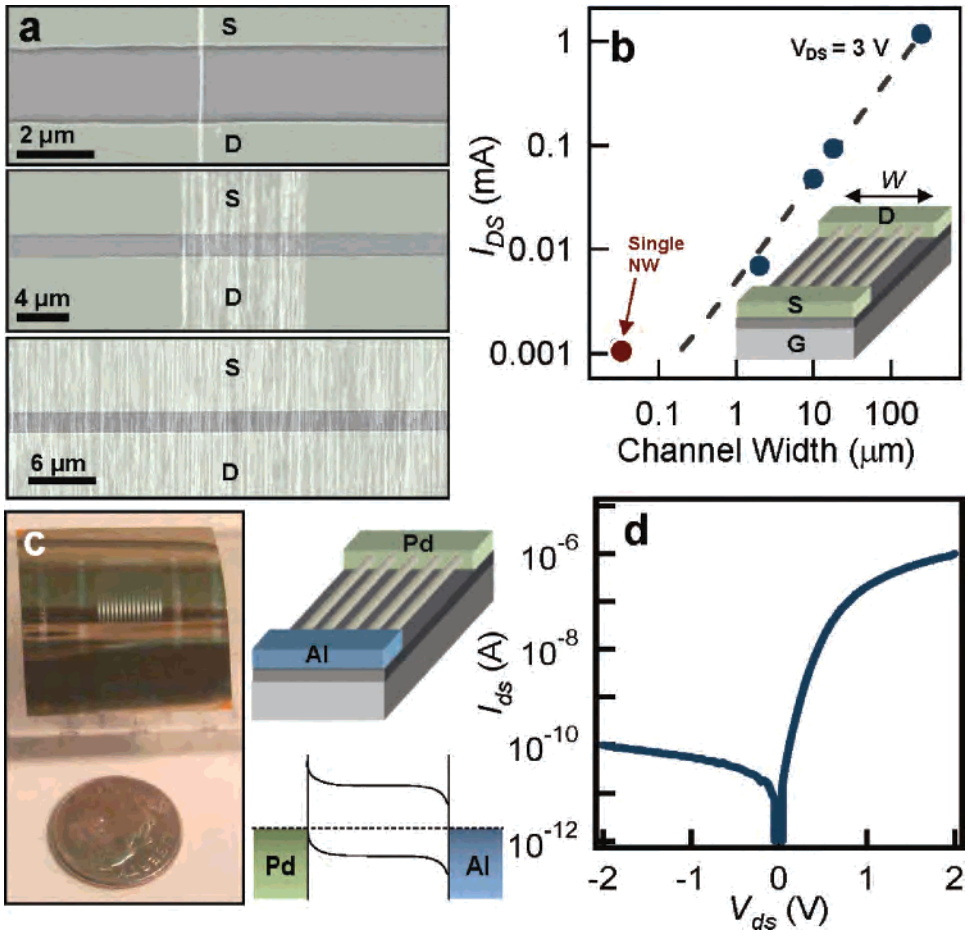

Figure 5. Devices based on printed nanowire arrays. (a) From top to bottom, SEM images of back-gated single NW FET, 10 μm and 250 μm wide parallel arrayed NW FETs. High mobility Ge/Si (15/5 nm) NWs were used as the channel material (see Supporting Information, Figure S2). (b) ON current as a function of channel width scaling, showing a highly linear trend. (c) Optical photograph and schematic of a novel diode structure fabricated on parallel arrays of p-SiNWs on a flexible plastic substrate. Asymmetric Pd−Al contacts are used to obtain Schottky diodes with the Pd forming a near ohmic contact to the valence band and Al resulting in a Schottky interface. (d) $I-V$ characteristic of a representative SiNW Schottky diode with a channel width ~250 μm and length ~3 μm.

scales with the channel width with a slope of ~5 μA/μm, corresponding to ~5 NW/μm since on average a single Ge/Si NW in an unoptimized back-gated geometry delivers ~1 μA. This NW density is consistent with the expected NW pitch of similar diameter and receiver substrate surface functionalization (Figure 2). It is worthy to note that in the future, the device performance can be readily improved by ~1−2 orders of magnitude through channel length scaling, and high-κ dielectric and metal top gate integration to enable better electrostatic modulation of the NWs as previously demonstrated for the case of single Ge/Si NW FETs.[32] The highly linear scaling of the ON current with the channel width demonstrates the uniformity and reproducibility of the well-aligned NW arrays that are enabled through our contacting printing process.

A unique aspect of our printing process is its compatibility with various substrate materials, including plastics. Figure 5c shows an optical photograph and schematic of the parallel array SiNW diodes that were fabricated on flexible plastic substrates (Kapton, DuPont). The printed p-SiNW arrays were configured into novel diode structures by using asymmetric Pd−Al S−D contacts. High work function Pd metal forms a near ohmic contact to the valence band of the p-SiNWs whereas low work function Al results in a Schottky contact. Notably, no doping profiling (for example, p−n junctions) of NWs is used for obtaining the diodes. This is critical since such an extrinsic doping process requires high-temperature diffusion and/or activation of the dopants which is not compatible with the plastic substrates. The $I-V$ characteristic of a representative NW Schottky diode is shown in Figure 5d, demonstrating clear rectifying effect with 4 orders of magnitude difference in the current for the reverse versus forward bias condition. The ability to readily obtain diode arrays based on crystalline semiconductor materials on plastic substrates is of significant interest for a wide range of potential optoelectronic applications, including solar cells, light emitting diodes, and light sensors.

In summary, a generic approach was developed to directly transfer regular arrays of semiconductor NWs from donor to patterned receiver substrates. The transferred NWs are highly ordered and aligned, enabling the assembly of both single NWs and densely packed parallel arrays of NWs with high uniformity across an entire wafer. In addition, various device structures, such as field-effect transistors with single and parallel arrays of NWs and Schottky diodes with asymmetric contacts were fabricated on rigid and flexible

substrates, demonstrating the potency and versatility of our method for integrating NW materials for electronic applications.

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Supporting Information Available: Procedures for surface modification, nanowire growth, and contact printing and detailed studies on the role of lubricant in the transfer process. This material is available free of charge via the Internet at http://pubs.acs.org.

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Supporting Information

NANOWIRE GROWTH

Si, Ge and core/shell Ge/Si NWs were grown in a custom built CVD system using previously reported vapor-liquid-solid process. Monodispersed gold nanoparticles with d=10-100 nm (Ted Pella, Inc.) were used as catalytic seeds on a Si/SiO_2 (50 nm) substrates. The typical surface density of the deposited Au nanoparticles was ~20 μm^{-2}. *p*-type SiNWs were grown at 460 ºC and 30 torr pressure under a constant flow of silane (4 s.c.c.m.), hydrogen (15 s.c.c.m.), and diborane (0.01% balanced H_2, 5 s.c.c.m.) for 15 minutes, resulting in ~120 μm long NWs. GeNWs were grown at 280 ºC and 45 torr with the use of germane (10% balanced in H_2, 15 s.c.c.m.) as the precursor gas. Under this growth condition, a growth rate of ~ 1 μm/min was observed. Core/shell Ge/Si NWs were synthesized by depositing a thin crystalline Si shell (~ 5nm) on the GeNWs that were grown using the above condition. The Si shell was deposited at 430 ºC under a flow of 2 s.c.c.m. SiH_4 and 15 s.c.c.m. H_2 at 2.8 torr for 10 minutes.

SURFACE FUNCTIONALIZATION OF RECIEVER SUBSTRATES

Surface modification of Si/SiO_2 (50 nm) substrates was achieved by well-established siloxane-based condensation chemistry of various compounds including (heptadecafluoro-1,1,2,2-tetrahydrodecyl) dimethylchlorosilane (Gelest, Inc.), N-trimethoxysilylpropyl-N,N,N-trimethylammonium chloride (Gelest, Inc.), and 3-Triethoxysilylpropylamine (Sigma-Aldrich, Inc.) to define $-CF_3$, $-N(Me)_3^+$, or $-NH_2$ terminated surfaces, respectively. To carry out the reactions, solutions of ~0.5 vol% of the above compounds were prepared with either hexane or ethanol as the solvent. Si/SiO_2 substrates were then reacted with the respective solutions for 45 min, followed by a

thorough wash with the solvent and baking at 120ºC for 20 min. For the poly-L-lysine functionalization, the substrate was coated with ~0.1% w/v of poly-L-lysine in water (Ted Pella, Inc.) for 5 min, and was then thoroughly rinsed with DI water. Notably, the poly-L-lysine functionalization can be carried out directly on top of the photolithographically patterned substrate since it does not react with the Shipley 1805 photoresist.

NANOWIRE PRINTING

The receiver substrate was patterned by photo (Shipley, 1805 resist) or electron beam lithography (PMMA 495 C2, diluted 50% in chlorobenzene) to define the assembly regions with the desired width and length, and was then mounted on a fixed stage and covered with a 2:1, *v*:*v* mixture of octane and mineral oil to serve as a lubricant. The donor (growth) substrate, consisting of a lawn of NWs was cut into the desired dimension and mounted on a metal weight. The weight was chosen so that it provides a pressure of ~ 10 g/cm^2. The donor chip, along with the weight, was then gently brought into contact on the receiver substrate, such that the donor and receiver substrates directly face each other with the edge of the donor chip ~0.5 mm away from the edge of the pattern of the receiver substrate. The weight, and therefore the donor substrate, was then pushed by a micromanipulator for ~0.5 mm with a constant velocity of ~20 mm/min in the direction parallel to the resist patterns of the receiver substrate. A second weight was then added to the donor chip in order to increase the total pressure to ~20 g/cm^2. The sliding was then continued with the same velocity of ~20 mm/min until the donor chip passed over the entire pattern of the receiver substrate. The donor chip and the weights were then gently

removed and the receiver substrate was rinsed well in octane. Note that our double weight approach is used to avoid mechanical "stamping" of NWs at the initial stage when the two substrates are brought in contact. Important care was taken to ensure no dust particles were found on either of the two substrates prior to the contact printing process. For all of our presented contact printing results, we used donor substrates with high NW density (>10 NW/μm^2).

NANOWIRE ARRY DEVICE FABRICATION AND CHARACTERIZATION

Source/drain electrodes were patterned with photolithography (Karl Suss MA6 Mask Aligner) on top of the contact printed NWs on both Kapton (DuPont) and Si/SiO_2 substrates, followed by lift-off. For Ge/Si NW array FETs, Ni (5nm)/Pd(45nm) metal films were deposited by electron beam evaporation. The spacing between source and drain electrodes is ~2 μm. For the electrical measurements, heavily doped Si substrate was used as a global back-gate. For SiNW Schottky diodes, two separate lithography and metallization processes were carried out to obtain Pd (50 nm) and Al (50 nm) asymmetric contacts on the printed SiNWs (d~30 nm) with a flexible Kapton substrate. The Kapton substrate was coated with SU8 (Shipley) followed by deposition of ~25 nm SiO_2 (e-beam evaporation) to improve the surface quality for contact printing. The surface was then coated with poly-L-lysine to enhance the printed NW density. After fabrication, the electrical transport properties of the devices were investigated with a probe station system (Signatone) and semiconductor parameter analyzer (Agilent 4155C) at room temperature.

THE ROLE OF LUBRICANT

Through systematic studies, we have explored the role of lubricant (2:1, *v*:*v* octane and mineral oil mixture) on the contact printing of nanowires. We find that the use of lubricant is essential for achieving highly dense, long, and well aligned parallel arrays of nanowires (Fig. S1). The lubricant serves as a spacing layer, minimizing the friction between the receiver and donor substrates, and NW-NW interactions; therefore, reducing the uncontrolled transfer of the nanowires due to mechanical coupling. This is quite evident in the surface functionalization studies, where significantly lower density contrast is observed for the dry transfer as compared to the lubricated transfer (Fig S1e). For instance, for the fluorinated (highly non-sticky) receiver substrates, which show weak chemical bonding interactions with nanowires, a density of $<10^{-3}$ NW/μm is obtained when lubricant is used while a density of ~ 2NW/μm is observed for the dry printing.

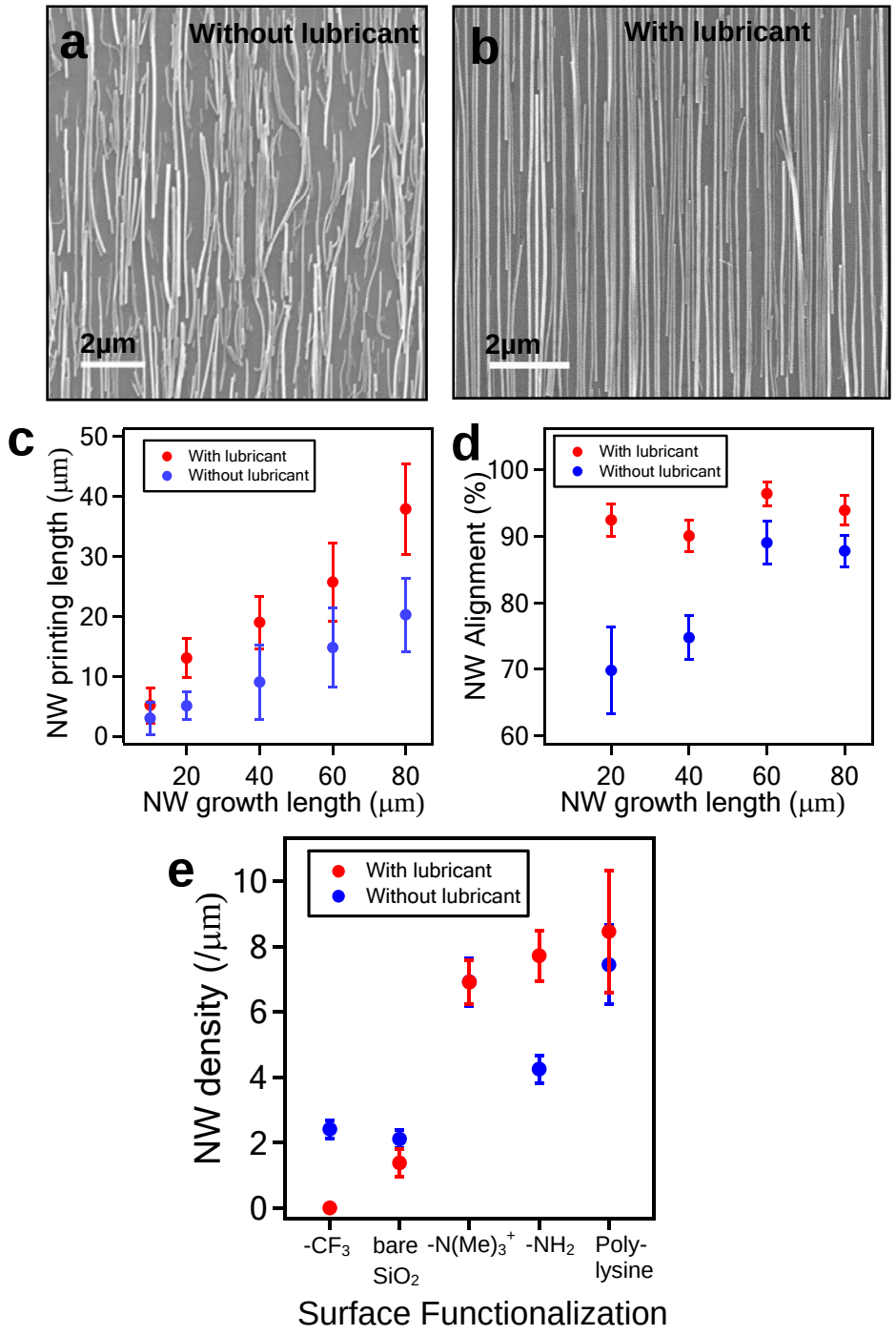

Figure S1. The effect of lubricant on the contact printing of the nanowires. SEM images of GeNW printing without (a) and with (b) lubricant, clearly showing the impact of the lubricant in obtaining highly aligned and ordered NWs. (c) The average length and (d) orientation alignment of the printed GeNWs as a function of their original length on the growth substrate for contact printing with and without lubricant. For (a)-(d) the receiver substrate was functionalized with poly-L-lysine. (e) Nanowire printing density of GeNWs (d~15 nm) as a function of the surface functionalization of the receiver substrate.

ELECTRICAL CHARACTERIZATION OF PARALLEL ARRAY NW FETS

Core/shell Ge/Si nanowires were printed to form high density and well aligned parallel arrays. Subsequently, the NW arrays were used to fabricate back-gated FETs as shown in the main content. Figure S2 shows the electrical properties of a representative FET fabricated on a ~10 μm wide NW film, consisting of ~50 NWs (5 NWs/μm). It shows a clear *p*-type transistor behavior with a linear transconductance of ~2.3μA/V. The modest transconductance originates from the back gate structure with relatively thick gate dielectric (50 nm SiO_2), and in the future, it can be readily improved through high-k dielectric and metal top gate integration, and channel length scaling.[32]

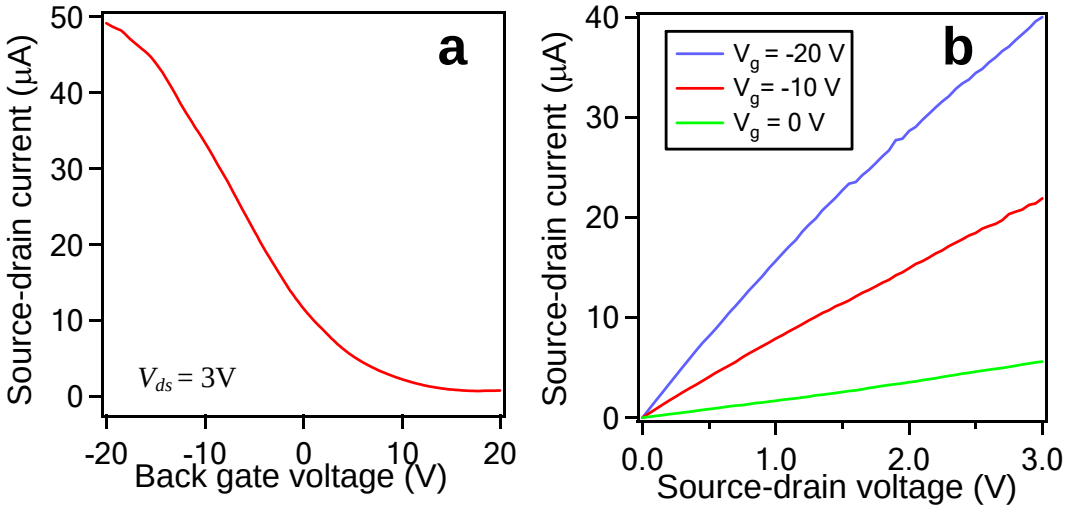

Figure S2. Electrical Characteristics of Ge/Si core/shell NWs. (a) I_{ds}-V_{gs} and (b) I_{ds}-V_{ds} characteristics of a representative FET fabricated on a parallel array of printed nanowires with a channel width of ~10 μm (~50 NWs).